

**COMPOSITION BASED ON NANOPARTICLES OR A NANOLATEX OF
POLYMERS FOR FABRIC CARE**

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5 The present invention relates to a
composition for fabric care, in particular for cotton-
based fabrics, comprising nanoparticles or a nanolatex
of a polymer which is insoluble under the direct and/or
indirect working conditions of the said composition in
an aqueous or wet medium.

10 The expression "fabric care" means the
protection of fabrics against physical or chemical
degradation phenomena and/or the provision of benefits
thereto, for instance softening and/or crease-
resistance properties.

15 The machine washing of fabrics leads to a
physical and chemical degradation of the fibres and
most particularly of cotton fibres. The alkalinity
delivered by detergents and also by certain specific
compounds such as oxidizing substances (perborate or
20 percarbonate) or certain enzymes may be the cause of
the chemical degradation of cotton fibres. However, it
is generally the combination of the chemical and
mechanical actions which leads to degradation of the
fibres. The mechanical action is produced during the
25 washing, rinsing, spin-drying or tumble-drying, when
the latter takes place in a tumble dryer. This
degradation of the fibres leads to the formation of

fibrils at the surface of the textile which end up causing coloured textiles to lose their radiance. This degradation also induces a decrease in the strength of the textile which, at the extreme, may lead to tearing
5 of the fabrics. This degradation of textiles may be evaluated quantitatively either by a loss of the colours of coloured textiles or by a reduction in the tear strength of the textile. It is generally necessary to carry out 10 to 20 cumulative machine washes in
10 order to perceive this type of degradation.

Cleaning in a washing machine, which systematically includes a spin-drying operation, also leads to creased fabrics, which is accentuated during the tumble-drying stage, in particular by the formation
15 of inter-fibre hydrogen bonds. It is thus necessary to iron the fabrics in order to make them look presentable.

In order to reduce the degradation of the fibres during washing or rinsing, the suppliers of
20 chemical products or detergents have made use of changes in detergent formulations or have used certain specific additives.

Mention may be made in particular of detergents comprising no oxidizing system, but which
25 have reduced cleaning capacities.

Silicone-based compounds have also been used, and in particular aminosilicones (US-A-4 585 563; WO 92/07927; WO 98/39401).

5 The Applicant has found that the use, in compositions for treating fabrics, in particular cotton-based fabrics, of nanoparticles or of a nanolatex of insoluble polymers makes it possible to prevent the degradation of the fabrics and/or to give them crease-resistance and/or softening properties.

10 Such compositions may especially be compositions for washing and/or rinsing and/or softening fabrics, for destaining fabrics before washing ("prespotting"), for tumble-drying wet fabrics in a tumble dryer or for ironing fabrics.

15 According to the invention, the expression "polymer nanoparticles" means particles with a diameter from about 10 to 500 nm, preferably from 20 to 300 nm, most particularly from 20 to 100 nm and even more particularly from 20 to 50 nm.

20 The expression "polymer nanolatex" means a stable aqueous dispersion of solid polymer nanoparticles with a mean size from about 10 to 500 nm, preferably from 20 to 300 nm, most particularly from 20 to 100 nm and even more particularly from 20 to 50 nm. Such a
25 dispersion generally has a solids content from about 10% to 50% by weight and preferably from about 20% to 40% by weight.

A first subject of the invention consists of a composition for fabric care, characterized in that it comprises nanoparticles or at least one nanolatex of at least one polymer (P) which is insoluble under the
5 working conditions of the said composition in an aqueous or wet medium.

A second subject of the invention consists of a process for fabric care by treating these fabrics with a composition, in an aqueous or wet medium,
10 comprising nanoparticles or at least one nanolatex of at least one polymer (P) which is insoluble in the said medium.

A third subject of the invention consists of the use, in a composition for treating fabrics in an aqueous or wet medium, of nanoparticles or of at least
15 one nanolatex of at least one polymer (P) which is insoluble in the said medium, as an agent for fabric care.

The composition and the working (or
20 treatment) conditions may be in numerous forms.

The said composition may be

* in the form of a solid (powder, granules, tablets, etc.) or of a concentrated aqueous dispersion, placed in contact with the fabrics to be treated, after
25 dilution in water;

* in the form of a concentrated dispersion placed beforehand on the dry fabrics to be treated before dilution in water;

* in the form of an aqueous dispersion to be placed directly on the dry fabrics to be treated without dilution or of a solid support (stick) comprising the said nanoparticles or the said nanolatex, to be applied directly to the dry fabrics to be treated;

* in the form of an insoluble solid support comprising the said nanoparticles or the said nanolatex of polymer (P) placed directly in contact with the wet fabrics to be treated.

Thus, the composition of the invention may be:

- a solid or liquid detergent formulation capable of directly forming a washing bath by dilution;
- a liquid rinsing and/or softening formulation capable of directly forming a rinsing and/or softening bath by dilution;
- a solid material, in particular a textile, comprising the said nanoparticles or the said nanolatex, which is intended to be placed in contact with wet fabrics in a tumble dryer (the said solid material is referred to hereinbelow as a "tumble dryer additive");
- an aqueous ironing formulation;

- a washing additive ("prespotter") intended to be placed on the dry fabrics prior to a washing operation using a detergent formulation containing or not containing the said nanoparticles or the said nanolatex (the said additive is referred to hereinbelow as a "prespotter").

The composition of the invention is particularly suitable for fabric care, especially for cotton-based fabrics, in particular fabrics containing at least 35% cotton.

The said polymer (P) preferably has a glass transition temperature T_g from about -40°C to 150°C , preferably from about 0 to 100°C and most particularly from about 10 to 80°C .

The term "polymer" means either a homopolymer or a copolymer derived from two or more monomers.

For good implementation of the invention, the said polymer (P) comprises:

- hydrophobic monomer units (N) that are uncharged or non-ionizable at the working pH of the composition of the invention,

- optionally at least one hydrophilic monomer unit (F) chosen from monomer units

* (F1) that are cationic or cationizable at the working pH of the said composition,

* (F2) that are amphoteric at the working pH of the said composition,

* (F3) that are anionic or anionizable at the working pH of the said composition,

* (F4) that are uncharged or non-ionizable, of hydrophilic nature, at the working pH of the said composition,

* or mixtures thereof

- and optionally at least one crosslinking unit (R).

The said monomer units (N) and (F) are preferably derived from α - β monoethylenically unsaturated monomers.

The said monomer units (R) are preferably derived from diethylenically unsaturated monomers.

The average molar mass of the said polymer (measured by gel permeation chromatography (GPC) THF and expressed as polystyrene equivalents) may preferably be at least 20 000.

As examples of monomers from which the hydrophobic units (N) are derived, mention may be made of:

- vinylaromatic monomers such as styrene, vinyltoluene, etc.,
- alkyl esters of α - β monoethylenically unsaturated acids such as methyl, ethyl, etc. acrylates and methacrylates,
- vinyl or allylic esters of saturated carboxylic acids, such as vinyl or allyl acetates, propionates or versatates,

- α - β monoethylenically unsaturated nitriles, such as acrylonitrile, etc.

As examples of monomers from which the cationic or cationizable hydrophilic units (F1) are derived, mention may be made of:

- N,N-(dialkylamino- ω -alkyl)amides of α - β monoethylenically unsaturated carboxylic acids such as N,N-dimethylaminomethyl acrylamide or methacrylamide, N,N-dimethylaminoethyl acrylamide or methacrylamide, N,N-dimethylamino-3-propyl acrylamide or methacrylamide and N,N-dimethylaminobutyl acrylamide or methacrylamide,
- α - β monoethylenically unsaturated amino esters, such as dimethylaminoethyl methacrylate (DMAM), dimethylaminopropyl methacrylate, di-tert-butylaminoethyl methacrylate or dipentylaminoethyl methacrylate,
- monomers that are precursors of amine functions, such as N-vinylformamide, N-vinylacetamide, etc., which generate primary amine functions by simple acidic or basic hydrolysis.

As examples of monomers from which the amphoteric hydrophilic units (F2) are derived, mention may be made of:

- N,N-dimethyl-N-methacryloyloxyethyl-N-(3-sulphopropyl)ammonium sulphobetaine (SPE from Raschig), N,N-dimethyl-N-(2-methacrylamidoethyl)-N-(3-sulphopropyl)ammonium betaine (SPP from Raschig), 1-vinyl-

3-(3-sulphopropyl)imidazolidium betaine or
1-(3-sulphopropyl)-2-vinylpyridinium betaine (SPV
from Raschig),

- derivatives of the quaternization reaction of
- 5 N-(dialkylamino- ω -alkyl)amides of α - β ethylenically
unsaturated carboxylic acids, such as N,N-dimethyl-
aminomethyl acrylamide or methacrylamide,
N,N-dimethylamino-3-propyl acrylamide or methacryl-
amide, or ethylenically unsaturated amino esters,
10 such as di-tert-butylaminoethyl methacrylate or
dipentylaminoethyl methacrylate, with a chloroacetate
of an alkali metal (in particular sodium) or of
propane sultone.

15 As examples of monomers from which the
anionic or anionizable hydrophilic units (F3) are
derived, mention may be made of:

- monomers containing at least one carboxylic function,
such as α - β ethylenically unsaturated carboxylic
acids or anhydrides, acrylic, methacrylic, maleic,
20 fumaric or itaconic acids or anhydrides,
N-methacroylalanine or N-acryloylhydroxyglycine, and
water-soluble salts thereof,
- monomers containing at least one sulphate or
sulphonate function, such as 2-sulphooxyethyl
25 methacrylate, vinylbenzenesulphonic acid, allyl-
sulphonic acid, 2-acrylamido-2-methylpropanesulphonic
acid, sulphoethyl acrylate or methacrylate, or

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sulphopropyl acrylate or methacrylate, and water-soluble salts thereof,

- 5
- monomers containing at least one phosphonate or phosphate function, such as vinylphosphonic acid, esters of ethylenically unsaturated phosphates such as phosphates derived from hydroxyethyl methacrylate (Empicryl 6835 from Rhodia) and those derived from polyoxyalkylene methacrylates and water-soluble salts thereof,
 - 10 • α - β monoethylenically unsaturated monomers that are precursors of anionic function(s), such as those whose hydrolysis generates carboxylate functions (tert-butyl acrylate, dimethylaminoethyl acrylate, maleic anhydride, etc.).

15 As examples of monomers from which the uncharged or non-ionizable hydrophilic units (F4) are derived, mention may be made of:

- 20
- hydroxyalkyl esters of α - β ethylenically unsaturated acids, such as hydroxyethyl, hydroxypropyl, etc. acrylates and methacrylates,
 - α - β ethylenically unsaturated acid amides, such as acrylamide, N,N-dimethyl methacrylamide, N-methylol-acrylamide, etc.,
 - 25 • α - β ethylenically unsaturated monomers bearing a water-soluble polyoxyalkylenated segment of the polyethylene oxide type, such as polyethylene oxide α -methacrylates (Bisomer S20W, S10W, etc. from

Laporte) or α, ω -dimethacrylates, Sipomer BEM from Rhodia (polyoxyethylene ω -behenyl methacrylate), Sipomer SEM-25 from Rhodia (polyoxyethylene ω -tristyrylphenyl methacrylate), etc.,

- 5 • α - β ethylenically unsaturated monomers that are precursors of hydrophilic units or segments, such as vinyl acetate, which, once polymerized, may be hydrolysed to generate vinyl alcohol units or polyvinyl alcohol segments,
- 10 • α - β ethylenically unsaturated monomers of ureido type and in particular methacrylamidoethyl-2-imidazolidinone (Sipomer WAM II from Rhodia).

As examples of monomers from which the crosslinking units (R) are derived, mention may be made of:

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- divinylbenzene
- ethylene glycol dimethacrylate
- allyl methacrylate
- methylenebis(acrylamide)

20 • glyoxal bis(acrylamide).

The said polymers (P) may be obtained in a known manner by free-radical polymerization in aqueous medium of ethylenically unsaturated monomers. The said nanolatices may be obtained in particular by free-

25 radical emulsion polymerization in water.

Processes for obtaining nanoparticulate latices of small diameter are described in Colloid

Polym. Sci. 266:462-469 (1988) and in Journal of Colloid and Interface Science. Vol. 89, No. 1, September 1982, pages 185 et seq. One method for preparing latices of particles with a mean size of less than 100 nm, in particular with a mean size ranging from 1 to 60 nm and most particularly from 5 to 40 nm, is described in EP-A-644 205.

The choice and relative amounts of the monomer(s) from which the unit(s) (N), (F) and (R) of the polymer (P) are derived are such that the said polymer (P) has a glass transition temperature T_g from about -40°C to 150°C , preferably from about 0 to 100°C and most particularly from about 10 to 80°C , and remains insoluble under the working conditions of the composition of the invention.

According to the invention, the said polymer (P) is considered as insoluble when less than 15% and preferably less than 10% of its weight is soluble in the aqueous or wet working medium of the composition of the invention, that is to say in particular under the temperature and pH conditions of the said medium.

The working pH for the composition of the invention may range from about 2 to about 12, depending on the desired use.

When it is

- a detergent formulation, the pH of the washing bath is generally from about 7 to 11 and preferably from 8 to 10.5;
- a rinsing and/or softening formulation, the pH of the
5 rinsing and/or softening bath is generally from about 2 to 8;
- a tumble dryer additive, the pH to be considered is that of the residual water, which may be from about 2 to 9;
- 10 - an aqueous ironing formulation, the pH of the said formulation is generally from about 5 to 9;
- a prespotter, the pH to be considered is that of the washing bath for the operation following the washing, namely from about 7 to 11 and preferably from 8 to
15 10.5.

For good implementation of the invention, at least 70% of the total mass of the said polymer (P) is formed from hydrophobic unit(s) (N).

When hydrophilic units (F) are present, they
20 preferably represent not more than 30% of the total mass of the polymer (P).

When crosslinking units (R) are present, they generally represent not more than 20%, preferably not more than 10% and most particularly not more than 5% of
25 the total mass of the polymer (P).

A first embodiment of the invention consists of a composition (C1) comprising nanoparticles or at

least one nanolatex of at least one uncharged or non-ionizable polymer (P1) comprising

- at least 70% of its weight of hydrophobic monomer units (N)
- 5 • optionally at least 1% of its weight of uncharged or non-ionizable hydrophilic monomer units (F4)
- optionally not more than 20% of its weight of uncharged or non-ionizable crosslinking units (R).

Preferably, according to this first
10 embodiment, the said uncharged or non-ionizable polymer (P1) comprises:

- at least 70% of its weight of hydrophobic monomer units (N)
- from 3% to 30% of its weight of uncharged or non-
15 ionizable hydrophilic monomer units (F4)
- optionally not more than 20% and preferably not more than 10% of its weight of uncharged or non-ionizable crosslinking units (R).

The said uncharged or non-ionizable polymer
20 (P1) may be used in any type of fabric care composition mentioned above, the working pH of which may range from 2 to 12, namely detergent formulations, rinsing and/or softening formulations, tumble dryer additives, aqueous ironing formulations or prespotters.

25 A second embodiment of the invention consists of a composition (C2) comprising nanoparticles or at least one nanolatex of at least one polymer (P2)

containing anionic or anionizable units and being free of cationic or cationizable units, comprising

- at least 70% of its weight of hydrophobic monomer units (N)
- 5 • at least 1% of its weight, preferably from 3% to 30% of its weight and most particularly from 1% to 20% of its weight, of anionic or anionizable hydrophilic monomer units (F3)
- optionally not more than 29% of its weight of
- 10 uncharged or non-ionizable hydrophilic monomer units (F4).

The said polymer (P2) can be used in fabric care compositions of non-cationic nature, namely detergent formulations, tumble dryer additives, aqueous

15 ironing formulations or prespotters.

- A third embodiment of the invention consists of a composition (C3) comprising nanoparticles or at least one nanolatex of at least one polymer (P3) containing amphoteric units, comprising
- 20 • at least 70% of its weight of hydrophobic monomer units (N)
 - at least 0.1% of its weight, preferably not more than 20% of its weight and most particularly not more than 10% of its weight, of amphoteric hydrophilic monomer
 - 25 units (F2)
 - optionally uncharged or non-ionizable hydrophilic monomer units (F4)

- optionally cationic or cationizable hydrophilic monomer units (F1),

the combination of hydrophilic monomer units (F)

preferably representing at least 1% of the weight of

- 5 the polymer (P3), and the molar ratio of the cationic charges to the anionic charges possibly ranging from 1/99 to 80/20 depending on the desired use of the said composition (C3).

10 The said polymer (P3) with a molar ratio of the cationic charges to the anionic charges ranging from 1/99 to 80/20 may be used in tumble dryer additives and aqueous ironing formulations.

15 The said polymer (P3) with a molar ratio of the cationic charges to the anionic charges ranging from 1/99 to 60/40 and preferably from 5/95 to 50/50 may also be used in detergent formulations and prespotters.

20 A fourth embodiment of the invention consists of a composition (C4) comprising nanoparticles or at least one nanolatex of at least one polymer (P4) containing both cationic or cationizable units and anionic or anionizable units, comprising

- at least 70% of its weight of hydrophobic monomer units (N)
- 25 • cationic or cationizable hydrophilic monomer units (F1)
- anionic or anionizable hydrophilic monomer units (F3)

- optionally amphoteric hydrophilic monomer units (F2)
- optionally uncharged or non-ionizable hydrophilic monomer units (F4),

the combination of hydrophilic monomer units (F)

5 preferably representing at least 1% of the weight of the polymer (P4), and the molar ratio of the cationic charges to the anionic charges possibly ranging from 1/99 to 80/20 depending on the desired use of the said composition (C4).

10 The said polymer (P4) with a molar ratio of the cationic charges to the anionic charges ranging from 1/99 to 80/20 may be used in tumble dryer additives and aqueous ironing formulations.

15 The said polymer (P4) with a molar ratio of the cationic charges to the anionic charges ranging from 1/99 to 60/40 and preferably from 5/95 to 50/50 may also be used in detergent formulations and prespotters.

20 A fifth embodiment of the invention consists of a composition (C5) comprising nanoparticles or at least one nanolatex of at least one polymer (P5) containing cationic or cationizable units and being free of anionic or anionizable units, comprising

- at least 70% of its weight of hydrophobic monomer units (N)
- at least 1% of its weight, preferably from 3% to 30% of its weight and most particularly from 1% to 10% of

25

its weight, of cationic or cationizable hydrophilic monomer units (F1)

- optionally not more than 20% of its weight of uncharged or non-ionizable hydrophilic monomer units (F4).

The said polymer (P5) may be used in any type of fabric care composition mentioned above, the working pH of which may range from 2 to 12, namely detergent formulations, rinsing and/or softening formulations, tumble dryer additives, aqueous ironing formulations or prespotters.

In a most preferred manner, when the composition (C5) is a detergent composition, the said monomer units (F1) are cationizable units derived from at least one cationizable monomer with a pKa of less than 11 and preferably of less than 10.5.

As examples of nanoparticles or a nanolatex of polymer (P), mention may be made in particular of nanoparticles or a nanolatex of copolymers containing units derived from

* methyl methacrylate/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid, the glass transition temperature Tg of which may range from 10°C to 80°C, depending on the composition of the said polymer

* methyl methacrylate/ethylene glycol dimethacrylate/methacrylic acid, the glass transition temperature Tg

of which may range from 10°C to 80°C, depending on the composition of the said polymer

* styrene/divinylbenzene/methacrylic acid, the glass transition temperature T_g of which may range from 100°C to 140°C, depending on the composition of the said polymer

* styrene/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid, the glass transition temperature T_g of which may range from 10°C to 80°C, depending on the composition of the said polymer

* Veova 10 (vinyl C₁₀ versatate)/methyl methacrylate/butyl acrylate/methacrylic acid, the glass transition temperature T_g of which may range from 10°C to 80°C, depending on the composition of the said polymer

* methyl methacrylate/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid/N,N-dimethyl-N-methacryloyloxyethyl-N-(3-sulphopropyl) ammonium sulphobetaine (SPE from Raschig), the glass transition temperature T_g of which may range from 10°C to 80°C, depending on the composition of the said polymer

* methyl methacrylate/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid/vinylphosphonic acid, the glass transition temperature T_g of which may range from 10°C to 80°C, depending on the composition of the said polymer

* methyl methacrylate/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid/Empicryl 6835 from

Rhodia, the glass transition temperature T_g of which may range from 10°C to 80°C, depending on the composition of the said polymer.

5 The amount of nanoparticles or of nanolatex of polymer (P) present in the care composition according to the invention may range from 0.05% to 10% as dry weight relative to the dry weight of the said composition, depending on the desired application.

10 Thus, the said polymer (P) may be used as follows:

% of nanoparticles or nanolatex of polymer (P) (as dry weight)	In a care composition according to the invention used as
0.05 - 5 preferably 0.1 - 3	detergent formulation
0.05 - 3 preferably 0.1 - 2	rinsing and/or softening formulation
0.05 - 10 preferably 0.1 - 5	tumble dryer additive
0.05 - 10 preferably 0.1 - 5	ironing formulation
0.05 - 10 preferably 0.1 - 5	prespotter

Other constituents may be present, along with the nanoparticles or the nanolatex of polymer (P), in the care composition according to the invention. The nature of these constituents depends on the desired use
15 of the said composition.

Thus, when it is a detergent formulation, for washing fabrics, it generally comprises:

- at least one natural and/or synthetic surfactant,
- 5 - at least one detergent adjuvant ("builder")
- optionally an oxidizing agent or system, and
- a series of specific additives.

The detergent formulation may comprise surfactants in an amount corresponding to about 3% to 40% by weight relative to the detergent formulation, these surfactants being such as

Anionic surfactants

- alkyl ester sulphonates of formula $R-CH(SO_3M)-COOR'$, in which R represents a C_8-C_{20} and preferably $C_{10}-C_{16}$ alkyl radical, R' represents a C_1-C_6 and preferably C_1-C_3 alkyl radical and M represents an alkali metal (sodium, potassium or lithium) cation, a substituted or unsubstituted ammonium (methyl-, dimethyl-, trimethyl- or tetramethylammonium, dimethylpiperidinium, etc.) or
- 15 an alkanolamine derivative (monoethanolamine, diethanolamine, triethanolamine, etc.). Mention may be made most particularly of methyl ester sulphonates in which the radical R is $C_{14}-C_{16}$;
- alkyl sulphates of formula $ROSO_3M$, in which R
- 25 represents a C_5-C_{24} and preferably $C_{10}-C_{18}$ alkyl or hydroxyalkyl radical, M representing a hydrogen atom or a cation of the same definition as above, and also the

ethoxylated (EO) and/or propoxylated (PO) derivatives thereof, containing on average from 0.5 to 30 and preferably from 0.5 to 10 EO and/or PO units;

• alkylamide sulphates of formula $RCONHR'OSO_3M$ in which

5 R represents a C_2-C_{22} and preferably C_6-C_{20} alkyl radical, R' represents a C_2-C_3 alkyl radical, M representing a hydrogen atom or a cation of the same definition as above, and also the ethoxylated (EO) and/or propoxylated (PO) derivatives thereof,

10 containing on average from 0.5 to 60 EO and/or PO units;

• saturated or unsaturated C_8-C_{24} and preferably $C_{14}-C_{20}$ fatty acid salts, C_9-C_{20} alkylbenzenesulphonates, primary or secondary C_8-C_{22} alkylsulphonates, alkyl-

15 glyceryl sulphonates, the sulphonated polycarboxylic acids described in GB-A-1 082 179, paraffin sulphonates, N-acyl N-alkyltaurates, alkyl phosphates, isethionates, alkyl succinamates, alkyl sulphosuccinates, sulpho-

20 succinate monoesters or diesters, N-acyl sarcosinates, alkylglycoside sulphates, polyethoxycarboxylates; the cation being an alkali metal (sodium, potassium or lithium), a substituted or unsubstituted ammonium residue (methyl-, dimethyl-, trimethyl- or tetramethyl-

25 ammonium, dimethylpiperidinium, etc.) or an alkanolamine derivative (monoethanolamine, diethanolamine, triethanolamine, etc.);

Nonionic surfactants

- 5 • polyoxyalkylenated (polyoxyethylenated, polyoxypropylenated or polyoxybutylenated) alkylphenols in which the alkyl substituent is C₆-C₁₂ and containing from 5 to 25 oxyalkylene units; examples which may be mentioned are the products Triton X-45, X-114, X-100 or X-102 sold by Rohm & Haas Co.;
- 10 • glucosamide, glucamide or glycerolamide;
- polyoxyalkylenated C₈-C₂₂ aliphatic alcohols containing from 1 to 25 oxyalkylene (oxyethylene or oxypropylene) units; examples which may be mentioned are the products Tergitol 15-S-9 and Tergitol 24-L-6 NMW sold by Union Carbide Corp., Neodol 45-9, Neodol 23-65, Neodol 45-7 and Neodol 45-4 sold by Shell Chemical Co., and Kyro
- 15 EOB sold by The Procter & Gamble Co.;
- products resulting from the condensation of ethylene oxide or the compound resulting from the condensation of propylene oxide with propylene glycol, such as the Pluronic products sold by BASF;
- 20 • products resulting from the condensation of ethylene oxide or the compound resulting from the condensation of propylene oxide with ethylenediamine, such as the Tetronic products sold by BASF;
- 25 • amine oxides such as C₁₀-C₁₈ alkyl dimethylamine oxides and C₈-C₂₂ alkoxy ethyl dihydroxyethylamine oxides;
- the alkylpolyglycosides described in US-A-4 565 647;
- C₈-C₂₀ fatty acid amides;

- 5
- ethoxylated fatty acids;
 - ethoxylated fatty amides;
 - ethoxylated amines.

Amphoteric and zwitterionic surfactants

- 5 • alkyl dimethylbetaines, alkylamidopropyl dimethylbetaines, alkyltrimethylsulphobetaines and the products of condensation of fatty acids and of protein hydrolysates;
- 10 • alkyl amphoacetates or alkyl amphodiacetates in which the alkyl group contains from 6 to 20 carbon atoms.

The detergent adjuvants ("builders") for improving the surfactant properties may be used in amounts corresponding to about 5-50% and preferably to about 5-30% by weight for the liquid detergent

15 formulations or to about 10-80% and preferably 15-50% by weight for the powder detergent formulations, these detergent adjuvants being such as:

Mineral detergent adjuvants

- 20 • polyphosphates (tripolyphosphates, pyrophosphates, orthophosphates or hexametaphosphates) of alkali metals, of ammonium or of alkanolamines
- tetraborates or borate precursors;
- silicates, in particular those with an $\text{SiO}_2/\text{Na}_2\text{O}$ ratio from about 1.6/1 to 3.2/1 and the lamellar silicates
- 25 described in US-A-4 664 839;
- alkali metal or alkaline-earth metal carbonates (bicarbonates, sesquicarbonates);

• cocranulates of alkali metal silicate hydrates and of alkali metal (sodium or potassium) carbonates that are rich in silicon atoms in Q2 or Q3 form, described in EP-A-488 868;

- 5 • crystalline or amorphous aluminosilicates of alkali metals (sodium or potassium) or of ammonium, such as zeolites A, P, X, etc.; zeolite A with a particle size of about 0.1-10 micrometers is preferred.

Organic detergent adjuvants

- 10 • water-soluble polyphosphonates (ethane 1-hydroxy-1,1-diphosphonates, methylenediphosphonate salts, etc.);
- water-soluble salts of carboxylic polymers or copolymers or water-soluble salts thereof, such as:
- 15 - polycarboxylate ethers (oxydisuccinic acid and its salts, monosuccinic acid tartrate and its salts, disuccinic acid tartrate and its salts);
- hydroxypolycarboxylate ethers;
- citric acid and its salts, mellitic acid and succinic acid and their salts;
- 20 - polyacetic acid salts (ethylenediaminetetraacetates, nitrilotriacetates, N-(2-hydroxyethyl)nitrilodiacetates);
- C₅-C₂₀ alkyl succinic acids and their salts (2-dodecenylsuccinates, lauryl succinates);
- 25 - carboxylic polyacetal esters;
- polyaspartic acid and polyglutamic acid and their salts;

- polyimides derived from the polycondensation of aspartic acid and/or of glutamic acid;
- polycarboxymethyl derivatives of glutamic acid or of other amino acids.

5 The detergent formulation may also comprise at least one oxygen-releasing bleaching agent comprising a percompound, preferably a persalt.

10 The said bleaching agent may be present in an amount corresponding to about 1% to 30% and preferably from 4% to 20% by weight relative to the detergent formulation.

15 As examples of percompounds which may be used as bleaching agents, mention should be made in particular of perborates such as sodium perborate monohydrate or tetrahydrate; peroxygenated compounds such as sodium carbonate peroxyhydrate, pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium peroxide and sodium persulphate.

20 The preferred bleaching agents are sodium perborate monohydrate or tetrahydrate and/or sodium carbonate peroxyhydrate.

25 The said agents are generally combined with a bleaching activator which generates, in situ in the washing medium, a peroxycarboxylic acid in an amount corresponding to about 0.1% to 12% and preferably from 0.5% to 8% by weight relative to the detergent formulation. Among these activators, mention may be

made of tetraacetylenediamine, tetraacetylmethylenediamine, tetraacetylglycoluril, sodium p-acetoxymethanesulphonate, pentaacetylglucose and octaacetyllactose.

5 Mention may also be made of non-oxygenated bleaching agents, which act by photo-activation in the presence of oxygen, these being agents such as sulphonated aluminium and/or zinc phthalocyanins.

10 The detergent formulation may also comprise soil-release agents, anti-redeposition agents, chelating agents, dispersants, fluorescers, foam suppressants, softeners, enzymes and various other additives.

Soil-release agents

15 These may be used in amounts of about 0.01-10%, preferably about 0.1-5% and more preferably about 0.2-3% by weight.

Mention may be made more particularly of agents such as:

- 20 • cellulose derivatives such as cellulose hydroxy ethers, methylcellulose, ethylcellulose, hydroxypropylmethylcellulose or hydroxybutylmethylcellulose;
- polyvinyl esters grafted onto polyalkylene trunks,
- 25 such as polyvinyl acetates grafted onto polyoxyethylene trunks (EP-A-219 048);
- polyvinyl alcohols;

- polyester copolymers based on ethylene terephthalate and/or propylene terephthalate and polyoxyethylene terephthalate units, with an ethylene terephthalate and/or propylene terephthalate (number of units)/
5 polyoxyethylene terephthalate (number of units) molar ratio from about 1/10 to 10/1 and preferably from about 1/1 to 9/1, the polyoxyethylene terephthalates containing polyoxyethylene units with a molecular weight from about 300 to 5 000 and preferably from
10 about 600 to 5 000 (US-A-3 959 230, US-A-3 893 929, US-A-4 116 896, US-A-4 702 857, US-A-4 770 666);
- sulphonated polyester oligomers obtained by sulphonation of an oligomer derived from ethoxylated allylic alcohol, from dimethyl terephthalate and from
15 1,2-propylene diol, containing from 1 to 4 sulphonated groups (US-A-4 968 451);
- polyester copolymers based on propylene terephthalate and polyoxyethylene terephthalate units and ending with ethyl or methyl units (US-A-4 711 730) or polyester
20 oligomers ending with alkylpolyethoxy groups (US-A-4 702 857) or sulphopolyethoxy (US-A-4 721 580) or sulphoaroyl (US-A-4 877 896) anionic groups;
- sulphonated polyester copolymers derived from terephthalic, isophthalic and sulphoisophthalic acid,
25 anhydride or diester and from a diol (FR-A-2 720 399).

Anti-redeposition agents

These may be used in amounts generally of about 0.01-10% by weight for a powder detergent formulation or about 0.01-5% by weight for a liquid detergent formulation.

Mention may be made in particular of agents such as:

- ethoxylated monoamines or polyamines, and ethoxylated amine polymers (US-A-4 597 898, EP-A-11 984);
- carboxymethylcellulose;
- sulphonated polyester oligomers obtained by condensation of isophthalic acid, dimethyl sulphosuccinate and diethylene glycol (FR-A-2 236 926);
- polyvinylpyrrolidones.

Chelating agents

Agents for chelating iron and magnesium may be present in amounts of about 0.1-10% and preferably of about 0.1-3% by weight.

Mention may be made, inter alia, of:

- aminocarboxylates such as ethylenediaminetetraacetates, hydroxyethylethylenediaminetriacetates and nitrilotriacetates;
- aminophosphonates such as nitrilotris(methylene-phosphonates);
- polyfunctional aromatic compounds such as dihydroxydisulphobenzenes.

Polymeric dispersants

These may be present in an amount of about 0.1-7% by weight, to control the calcium and magnesium hardness, these being agents such as:

- 5 · water-soluble polycarboxylic acid salts with a molecular mass from about 2 000 to 100 000, obtained by polymerization or copolymerization of ethylenically unsaturated carboxylic acids such as acrylic acid, maleic acid or anhydride, fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid or methylenemalononic acid, and most particularly polyacrylates with a molecular mass from about 2 000 to 10 000 (US-A-3 308 067), copolymers of ^{acrylic}~~maleic~~ acid and of maleic anhydride with a molecular mass from about 5 000 to 75 000 (EP-A-66 915);
- 10 15 · polyethylene glycols with a molecular mass from about 1 000 to 50 000.

Fluorescers (brighteners)

- These may be present in an amount of about 0.05-1.2% by weight, these being agents such as:
- 20 stilbene, pyrazoline, coumarin, fumaric acid, cinnamic acid, azole, methinecyanin, thiophene, etc. derivatives ("The production and application of fluorescent brightening agents" - M. Zahradnik, published by John Wiley & Sons, New York, 1982).
- 25

BDM 1-7-03

Foam suppressants

These may be present in amounts which may be up to 5% by weight, these being agents such as:

- C₁₀-C₂₄ monocarboxylic fatty acids or alkali metal, ammonium or alkanolamine salts thereof, and fatty acid triglycerides;
- saturated or unsaturated aliphatic, alicyclic, aromatic or heterocyclic hydrocarbons, such as paraffins and waxes;
- N-alkylaminotriazines;
- monostearyl phosphates and monostearyl alkyl phosphates;
- polyorganosiloxane oils or resins optionally combined with silica particles.

15 Softeners

These may be present in amounts of about 0.5-10% by weight, these being agents such as clays.

Enzymes

These may be present in an amount which may be up to 5 mg by weight and preferably of about 0.05-3 mg of active enzyme/g of detergent formulation, these being enzymes such as:

- proteases, amylases, lipases, cellulases and peroxidases (US-A-3 553 139, US-A-4 101 457, US-A-4 507 219, US-A-4 261 868).

Other additives

Mention may be made, inter alia, of:

- buffers,
- fragrances,
- pigments.

The detergent formulation may be used, in particular in a washing machine, in a proportion of from 0.5 g/l to 20 g/l and preferably from 2 g/l to 10 g/l to carry out washing operations at a temperature from about 25 to 90°C.

A second embodiment of the care composition of the invention consists of an aqueous liquid formulation for rinsing and/or softening fabrics.

It may be used in a proportion of from 0.2 to 10 g/l and preferably from 2 to 10 g/l.

Along with the nanoparticles or the nanolatex of polymer (P), there may be present other constituents of the type such as:

- combinations of cationic surfactants (triethanolamine diester quaternized with dimethyl sulphate, N-methylimidazoline tallow ester methyl sulphate, dialkyl-dimethylammonium chloride, alkylbenzyldimethylammonium chloride, methyl alkylimidazolinium sulphate, methyl methylbis(alkylamidoethyl)-2-hydroxyethylammonium sulphate, etc.) in an amount which may range from 3% to 50% and preferably from 4% to 30% of the said formulation, optionally combined with nonionic surfactants (ethoxylated fatty alcohols, ethoxylated alkylphenols, etc.) in an amount which may be up to 3%;

- optical brighteners (0.1% to 0.2%);
- optionally, colour-fast agents (polyvinylpyrrolidone, polyvinylloxazolidone, polymethacrylamide, etc. 0.03% to 25% and preferably 0.1% to 15%),
- 5 - colorants,
- fragrances,
- solvents, in particular alcohols (methanol, ethanol, propanol, isopropanol, ethylene glycol or glycerol),
- foam limiters.

10 A third embodiment of the care composition of the invention consists of an additive for drying fabrics in a suitable tumble dryer.

 The said additive comprises a flexible solid support consisting, for example, of a strip of woven or
15 nonwoven textile or a sheet of cellulose, comprising nanoparticles or impregnated with the nanolatex of polymer (P); the said additive is introduced at the time of tumble-drying into the wet fabrics to be dried at a temperature from about 50 to 80°C for 10 to
20 60 minutes.

 The said additive may also comprise cationic softeners (up to 99%) and colour-fast agents (up to 80%), such as those mentioned above.

 A fourth embodiment of the care composition
25 of the invention consists of an ironing formulation which may be sprayed directly onto the dry fabrics before ironing.

The said formulation may also contain silicone-based polymers (from 0.2% to 5%), nonionic surfactants (from 0.5% to 5%) or anionic surfactants (from 0.5% to 5%), fragrances (0.1% to 3%) or cellulose derivatives (0.1% to 3%), for instance starch; spraying the said formulation onto the fabrics makes it easier to iron them and limits the creasing of the fabrics when they are worn.

A fifth embodiment of the care composition of the invention consists of a prespotter which is in the form of an aqueous dispersion or a solid (stick).

Along with the nanoparticles or the nanolatex of polymer (P), there may be present other constituents of the type such as:

- anionic surfactants such as those already mentioned above, in an amount of at least 5% of the weight of the composition
- nonionic surfactants such as those already mentioned above, in an amount which may range from 15% to 40% of the weight of the composition
- aliphatic hydrocarbons, in an amount which can range from 5% to 20% of the weight of the composition.

A second subject of the invention consists of a process for caring for fabrics by treating them with a composition, in an aqueous or wet medium, comprising at least nanoparticles or a nanolatex of at least one polymer (P) that is insoluble in the said medium.

The type of composition, and also the amounts of polymer (P) and other additives which may be used, have already been mentioned above.

5 A third subject of the invention consists of the use, in a composition for treating fabrics in an aqueous or wet medium, of nanoparticles or of at least one nanolatex of at least one polymer (P) that is insoluble in the said medium, as a fabric care agent.

10 The type of composition, and also the amounts of polymer (P) and other additives which may be used, have already been mentioned above.

15 The said nanoparticles or the said nanolatex protect the fabrics in particular against physical or chemical degradation and/or give them benefits such as softening and/or crease-resistance properties.

The diameters of the nanoparticles or nanolatices of polymer according to the invention may be determined in a well-known manner by light scattering or by transmission electron microscopy.

20 The examples which follow are given for illustrative purposes.

The polymer (P) latices used to prepare the formulations in the examples of the invention are the latices (I) and (II) below:

25 Latex (I) of

* methyl methacrylate/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid/N,N-dimethyl-N-meth-

acryloyloxyethyl-N-(3-sulphopropyl)ammonium sulpho-
betaine (SPE from Raschig)

in a mass ratio between the various monomers of

42.3/35.4/15.8/4.2/2.2

5 the glass transition temperature Tg of which is about
41°C

having a mean particle size from about 35 to 45 nm
(determination by light scattering using a Malvern
Instrument Zetasizer machine) and a solids content of

10 about 30%.

Latex (II) of

* methyl methacrylate/butyl acrylate/hydroxyethyl
methacrylate/methacrylic acid,

in a mass ratio between the various monomers of

15 37/55/5/3

the glass transition temperature Tg of which is about
17°C

having a mean particle size from about 30 to 35 nm
(determination by light scattering using a Malvern

20 Instrument Zetasizer machine) and a solids content of
about 30%.

1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023 2024 2025 2026 2027 2028 2029 2030 2031 2032 2033 2034 2035 2036 2037 2038 2039 2040 2041 2042 2043 2044 2045 2046 2047 2048 2049 2050 2051 2052 2053 2054 2055 2056 2057 2058 2059 2060 2061 2062 2063 2064 2065 2066 2067 2068 2069 2070 2071 2072 2073 2074 2075 2076 2077 2078 2079 2080 2081 2082 2083 2084 2085 2086 2087 2088 2089 2090 2091 2092 2093 2094 2095 2096 2097 2098 2099 2100 2101 2102 2103 2104 2105 2106 2107 2108 2109 2110 2111 2112 2113 2114 2115 2116 2117 2118 2119 2120 2121 2122 2123 2124 2125 2126 2127 2128 2129 2130 2131 2132 2133 2134 2135 2136 2137 2138 2139 2140 2141 2142 2143 2144 2145 2146 2147 2148 2149 2150 2151 2152 2153 2154 2155 2156 2157 2158 2159 2160 2161 2162 2163 2164 2165 2166 2167 2168 2169 2170 2171 2172 2173 2174 2175 2176 2177 2178 2179 2180 2181 2182 2183 2184 2185 2186 2187 2188 2189 2190 2191 2192 2193 2194 2195 2196 2197 2198 2199 2200 2201 2202 2203 2204 2205 2206 2207 2208 2209 2210 2211 2212 2213 2214 2215 2216 2217 2218 2219 2220 2221 2222 2223 2224 2225 2226 2227 2228 2229 2230 2231 2232 2233 2234 2235 2236 2237 2238 2239 2240 2241 2242 2243 2244 2245 2246 2247 2248 2249 2250 2251 2252 2253 2254 2255 2256 2257 2258 2259 2260 2261 2262 2263 2264 2265 2266 2267 2268 2269 2270 2271 2272 2273 2274 2275 2276 2277 2278 2279 2280 2281 2282 2283 2284 2285 2286 2287 2288 2289 2290 2291 2292 2293 2294 2295 2296 2297 2298 2299 2300 2301 2302 2303 2304 2305 2306 2307 2308 2309 2310 2311 2312 2313 2314 2315 2316 2317 2318 2319 2320 2321 2322 2323 2324 2325 2326 2327 2328 2329 2330 2331 2332 2333 2334 2335 2336 2337 2338 2339 2340 2341 2342 2343 2344 2345 2346 2347 2348 2349 2350 2351 2352 2353 2354 2355 2356 2357 2358 2359 2360 2361 2362 2363 2364 2365 2366 2367 2368 2369 2370 2371 2372 2373 2374 2375 2376 2377 2378 2379 2380 2381 2382 2383 2384 2385 2386 2387 2388 2389 2390 2391 2392 2393 2394 2395 2396 2397 2398 2399 2400 2401 2402 2403 2404 2405 2406 2407 2408 2409 2410 2411 2412 2413 2414 2415 2416 2417 2418 2419 2420 2421 2422 2423 2424 2425 2426 2427 2428 2429 2430 2431 2432 2433 2434 2435 2436 2437 2438 2439 2440 2441 2442 2443 2444 2445 2446 2447 2448 2449 2450 2451 2452 2453 2454 2455 2456 2457 2458 2459 2460 2461 2462 2463 2464 2465 2466 2467 2468 2469 2470 2471 2472 2473 2474 2475 2476 2477 2478 2479 2480 2481 2482 2483 2484 2485 2486 2487 2488 2489 2490 2491 2492 2493 2494 2495 2496 2497 2498 2499 2500 2501 2502 2503 2504 2505 2506 2507 2508 2509 2510 2511 2512 2513 2514 2515 2516 2517 2518 2519 2520 2521 2522 2523 2524 2525 2526 2527 2528 2529 2530 2531 2532 2533 2534 2535 2536 2537 2538 2539 2540 2541 2542 2543 2544 2545 2546 2547 2548 2549 2550 2551 2552 2553 2554 2555 2556 2557 2558 2559 2560 2561 2562 2563 2564 2565 2566 2567 2568 2569 2570 2571 2572 2573 2574 2575 2576 2577 2578 2579 2580 2581 2582 2583 2584 2585 2586 2587 2588 2589 2590 2591 2592 2593 2594 2595 2596 2597 2598 2599 2600 2601 2602 2603 2604 2605 2606 2607 2608 2609 2610 2611 2612 2613 2614 2615 2616 2617 2618 2619 2620 2621 2622 2623 2624 2625 2626 2627 2628 2629 2630 2631 2632 2633 2634 2635 2636 2637 2638 2639 2640 2641 2642 2643 2644 2645 2646 2647 2648 2649 2650 2651 2652 2653 2654 2655 2656 2657 2658 2659 2660 2661 2662 2663 2664 2665 2666 2667 2668 2669 2670 2671 2672 2673 2674 2675 2676 2677 2678 2679 2680 2681 2682 2683 2684 2685 2686 2687 2688 2689 2690 2691 2692 2693 2694 2695 2696 2697 2698 2699 2700 2701 2702 2703 2704 2705 2706 2707 2708 2709 2710 2711 2712 2713 2714 2715 2716 2717 2718 2719 2720 2721 2722 2723 2724 2725 2726 2727 2728 2729 2730 2731 2732 2733 2734 2735 2736 2737 2738 2739 2740 2741 2742 2743 2744 2745 2746 2747 2748 2749 2750 2751 2752 2753 2754 2755 2756 2757 2758 2759 2760 2761 2762 2763 2764 2765 2766 2767 2768 2769 2770 2771 2772 2773 2774 2775 2776 2777 2778 2779 2780 2781 2782 2783 2784 2785 2786 2787 2788 2789 2790 2791 2792 2793 2794 2795 2796 2797 2798 2799 2800 2801 2802 2803 2804 2805 2806 2807 2808 2809 2810 2811 2812 2813 2814 2

Formulation	(A) with P	(B) colour without P	(C) without P
Constituents	% by weight	% by weight	% by weight
NaTPP	40		
Zeolite 4A	0	25	25
2 SiO ₂ , Na ₂ O silicate	5	5	5
Sodium carbonate	5	15	15
Acrylate/maleate copolymer Sokalan CP5 (BASF)	0	5	5
Sodium sulphate	8	21	8
CMC blanose 7MXF (Hercules)	1	1	1
Perborate monohydrate	15	0	15
Granulated TAED	5	0	5
Anionic surfactant Laurylbenzene sulphate (Nansa)	6	8	6
Nonionic surfactant Symperonic A3 (3 EO ethoxylated alcohol - ICI)	3	5	3
Nonionic surfactant Symperonic A9 (9 EO ethoxylated alcohol - ICI)	9	11	9

Formulation	(A) with P	(B) colour without P	(C) without P
Constituents	% by weight	% by weight	% by weight
Enzymes (esterases, amylases, cellulase, protease)	0.5	0.5	0.5
Fragrances	1	1	1
Latex (I) (% solids)	1.0	1.0	1.0
Polyvinylpyrrolidone	0	1	0
Soil-release sulphonated copolyester Repel-O-Tex PF 594 from Rhodia	0.5	0.5	0.5

A washing operation is carried out in a Tergotometer laboratory machine which is well known in the profession to detergent composition formulators. The machine simulates the mechanical and thermal effects of pulsating-type American washing machines, but, by virtue of the presence of 6 washing drums, it makes it possible to carry out simultaneous series of tests with an appreciable saving in time.

25 x 25 cm test pieces are cut from unfinished cotton. The cotton test pieces are first ironed so that they all have the same level of creasing before washing.

5 They are then washed using the above
detergent formulation containing latex (I) and rinsed
once, under the following conditions:

- number of test pieces per Tergotometer
drum: 2
- volume of water: 1 litre
- water of French hardness 30°TH obtained by
suitable dilution of Contrexéville® brand
mineral water
- washing product concentration: 5 g/l
- washing temperature: 40°C
- washing time: 20 min
- spin speed of the Tergotometer: 100 rpm
- rinsing with cold water (about 30°TH)
- rinsing time: 5 minutes

10
15 The test pieces are then creased under a 3 kg
press for 20 seconds, after which they are dried
vertically overnight.

20 The same operation is carried out using the
same detergent formulation, but free of latex (I).

A digital colour photograph is then taken of
the dry test pieces, which is then converted into
256 grey scale levels (grey scale from 0 to 255).

25 The number of pixels corresponding to each
grey scale level are counted.

For each histogram obtained, the standard deviation σ of the distribution of the grey scale level is measured.

σ_1 corresponds to the standard deviation obtained with the detergent formulation containing no latex.

σ_2 corresponds to the standard deviation obtained with the detergent formulation containing latex (I).

The performance value is given by the equation $-\Delta\sigma = \sigma_2 - \sigma_1$

The performance values obtained are as follows:

Formulation	(A)	(B)	(C)
$-\Delta\sigma$	3.5	4	4.5

These positive values of $-\Delta\sigma$ are representative of a crease-resistance property provided by the detergent formulation comprising the latex according to the invention.

Example 2

Rinsing/softening formulation

Constituents	% by weight
Cationic surfactant : ditallow dimethylammonium chloride	5%
Fragrance	1%
HCl to obtain a pH = 3	0.2%
Latex (I) or (II) (% solids)	2%